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PHOSPHORUS-CONTAINING DERIVATIVES OF DECABORANE(14) AS PRECURSORS OF BORON-CONTAINING MATERIALS

by

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A route to soluble boron-containing polymers has been developed. The synthesis and characterization of phosphorus-containing monomeric and polymeric derivatives of decaborane(14) ($B_{10}H_{14}$) are given. Preparation and characterization of boron-containing ceramic materials from these molecular and macromolecular species are discussed. Success has been achieved in the areas of ceramic fiber and monolith production and in the area of binder applications for composites of advanced ceramic materials.

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Phosphorus-Containing Derivatives of Decaborane(14) As Precursors to Boron-Containing Materials

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Introduction

Ceramic materials whose properties are attractive for high technology applications often fail to realize their full potential of usefulness due to an inability to be fabricated into complex, durable shapes.[1] One such class of materials is that of the boron-containing ceramics, *e.g.*, boron carbide, B_4C, boron nitride, BN, boron phosphides, BP, $B_{12}P_2$ and $B_{13}P_2$, aluminum boride, AlB_{12} and boron silicides, B_4Si, B_6Si, and $B_{12}Si$.[2] Boron carbide, one goal of our current effort, is ideally composed of B_{12} icosahedra interstitially linked by three carbon atoms, nominally producing B_4C stoichiometry; however, boron rich phases are also known. Crude boron carbide is prepared by the carbothermal reduction of B_2O_3, with or without added Mg; this material finds its primary use as an abrasive. Pure B_4C can be prepared either directly from the elements ($T>1600^oC$) or by reaction of $BCl_3/CCl_4/H_2$ gas phase mixtures at high temperatures. Material thus prepared has a density of 2.52 g/cm^3, mp of 2450^oC, and microhardness of 4.05 GPa. The neutron capture cross section area of the ^{10}B isotope is among the highest known.[3] Thus, its great hardness makes it attractive as ceramic armor plate, whereas its chemical inertness and radiation stability make it a candidate for nuclear applications. It will be appreciated that further development in these areas is inhibited by the inherent brittleness of the material, and lack of a suitable route to prepare it via a processable (*ie.* fusible and/or soluble) intermediate.

One method used to increase the fracture toughness (durability) of ceramic materials is to imbed a support of ceramic fibers or powder into a matrix (binder) of ceramic material. The resulting composite is strength reinforced relative to a single component system.[4] In previous work, we have developed polymeric silicon-containing systems whose pyrolytic conversion produces useful ceramic materials, silicon carbide, nitride, "carbonitride", or oxynitride, in high yield.[5] We now report the results of an effort to extend the use of preceramic polymers to boron-containing materials.[6] The motivation for this work was to utilize processable materials which give, in general, boron carbide as the major ceramic phase

upon pyrolysis. We will limit our current discussion to results obtained with phosphorus-containing molecular and macromolecular species. Three classes of compounds were explored, monomeric $L{\cdot}B_{10}H_{12}{\cdot}L$ species, phosphonium salts of $B_{10}H_{10}^{2-}$ and polymers of the general formula $\dagger B_{10}H_{12}{\cdot}L\sim\sim\sim L\dagger_x$.

Results and Discussion

Various known boron-containing systems were considered for possible use in this project. The need for the 4:1 boron to carbon ratio in B_4C led us to investigate the chemistry of the higher polyhedral boranes. Among these, $B_{10}H_{14}$ (Fig 1) is ideally suited for the preparation of polymers. A well-studied reaction of $B_{10}H_{14}$ is the substitution of neutral Lewis bases (electron pair donors) at the 6 and 9 positions, resulting in expulsion of one mole of H_2 and formation of a diadduct, $L{\cdot}B_{10}H_{12}{\cdot}L$ (Eq 1, Fig 2, Table S1). There is no gross polyhedral rearrangement during this reaction, the only structural change being the relocation of the B-H-B three-center, two-electron bridge bonds, upon going from one *nido* (open) structure to another. There are over 150 such $B_{10}H_{12}{\cdot}2L$ complexes reported in the literature.[7] On the whole, they are oxidatively, hydrolytically and thermally stable at ambient conditions. When the Lewis base employed is Et_3N, further reaction can occur upon heating the compound in a solution of boiling toluene to produce $[Et_3NH]_2[B_{10}H_{10}]$ (Fig 3, Table S1). This salt readily undergoes cation metathesis in aqueous solution (Eq 2).[8]

A difunctional Lewis base (:L~~~L:) should react with $B_{10}H_{14}$ to give polymeric species of type $\dagger B_{10}H_{12}{\cdot}L\sim\sim\sim L\dagger_x$ (Eq 3). Indeed, several such polymers already had been reported, for which :L~~~L: was $Et_2PCH_2CH_2PEt_2$,[9] Ph_2POPPh_2 "POP", and $Ph_2PN{=}PPh_2CH_2CH_2PPh_2{=}NPPh_2$ "PNP".[10]

We began our studies with the preparation of a number of $B_{10}H_{12}{\cdot}2L$ and $[cat]_2[B_{10}H_{10}]$ complexes (Table I). These can be divided into two classes: (1) Those which contain phenyl groups attached to phosphorus, whose pyrolysis (to 1000°C in an argon stream) gives a high (>70%) yield of ceramic residue. This residue contains a large fraction of the initial carbon content of the starting complex (*cf.* Table I). (This is a general characteristic of phenyl-containing preceramic polymers: see, for instance, ref 5). (2) Those which do not contain phenyl groups attached to phosphorus, whose pyrolysis gives lower (50-70%) yields of ceramic residue. Pyrolysis of powder samples (to 1000°C in an argon stream)

resulted in retention of considerable amounts of phosphorus (Table I); however, on further heating to 1500°C, nearly total loss of phosphorus occurred (Table IV) and B_4C was the only X-ray diffracting phase. In all cases, the ceramic residue from pyrolysis to 1000°C was amorphous. For similar experiments on monolithic samples, see the accompanying paper.[11]

These $B_{10}H_{12}{\cdot}2L$ and $[cat]_2[B_{10}H_{10}]$ complexes proved to be useful as binders for B_4C and other ceramic powders (SiC, BN, $B_{13}P_2$, Si_3N_4, B; Tables II, III and S1). The best results were obtained when the phosphorus ligand contained phenyl substituents, no doubt due to the high ceramic yields in these systems. Since, in this application, the boron-containing complexes used as binders are present in the composite sample to the extent of ~17% by weight (Table II), the excess of carbon in their pyrolytic char is less of a disadvantage than when the pure complexes (monoliths) are pyrolyzed. The excellent results obtained with boron powder (Table II) hint at a route useful for converting the excess carbon from the binder to B_4C. One known use of B_4C is as a densification aid (with or without added carbon) in silicon-containing ceramic materials; therefore we are encouraged by the results observed in this area (Table II).

Since our major interest was in applications involving ceramic monoliths and/or ceramic fibers (goals not realized with the above monomeric species), and polymeric species had filled these roles in our silicon-containing systems,[5] $B_{10}H_{14}$-derived polymers were of interest. In addition to the known POP and PNP polymers, we prepared new $\{B_{10}H_{12}{\cdot}L{\sim}{\sim}{\sim}L\}_x$ polymers derived from L~~~L= $Ph_2PCH_2PPh_2$ "PMP", $Ph_2PCH_2CH_2PPh_2$ "PEP", $Ph_2PCH_2CH_2CH_2PPh_2$ "PPP", $Ph_2PC{\equiv}CPPh_2$ "PCCP", and $Ph_2PNHNHPPh_2$ "PNNP", and studied their use as "preceramic polymers" (Table S1). Ceramic data (yield and elemental composition) for the pyrolysis products (1000°C, Ar atm) from these macromolecular species are in Table IV. The polymers containing POP, PMP, PEP, PPP and PCCP linkages served well both as binders for B_4C powder and, more importantly, in the production of ceramic monoliths by pyrolysis of shaped polymer bodies (Table S1). Of these, POP was the most successful and, therefore chosen as the target of a further, more detailed investigation.

Previous workers had determined the low temperature volatile byproducts of the pyrolysis of POP to consist of hydrogen and trace amounts of benzene.[10] We have determined the thermogravimetric (TGA/wt change) and thermomechanical (TMA/length change) properties of this polymer (Fig 4). The initial TGA weight loss arises from loss of H_2

caused by breakage of B-H bonds and concomitant formation of B-B bonds, as inferred from IR studies of the polymer prior to and after the weight loss. Likewise, intermediate weight loss is due to processes involving breakage of C-H bonds and formation of B-C bonds. High temperature weight loss is associated with loss of phosphorus. The TMA data imply that no melt phase is present for this polymer over the temperature range studied. By combining TMA and TGA measurements, a composite curve of density *vs* temperature may be calculated (Fig 5). These curves have been extended to higher temperatures.[11] The DRIFT (diffuse reflectance Fourier transform infrared) spectra of samples of POP polymer fired to 1000°C and 1500°C each showed broad absorptions at 780-830, 1090-1105 and 1560-1580 cm^{-1} attributed to the presence of B-B, B-C and C-C bonds, respectively. Additionally, the 1000°C sample had absorptions at 2850-3000 cm^{-1} attributed to the presence of residual B-H and C-H bonds.

Conclusions:

This work has demonstrated the usefulness of phosphorus-containing derivatives of decaborane(14) as precursors for boron-containing ceramic materials. All samples investigated served as binders for B_4C. The results of experiments employing $B_{10}H_{12}{\cdot}2L$ compounds and $[P^+]_2[B_{10}H_{10}]$ (P^+=phosphonium cation) salts in this capacity have been summarized; additionally, some complexes served well as binders for various other ceramic powders. The yield and elemental composition of ceramic materials derived from these molecular species and salts have been given. The best results were obtained when L was a diphenylphosphido derived Lewis base, presumably due to the high ceramic yields observed in these systems. Known, and new, polymers obtained from reactions of diphosphines with $B_{10}H_{14}$ have been shown to serve as ceramic powder binders, and, in some cases, as ceramic monolith precursors. Results of experiments using organic diamines in a similar manner, to yield either pure BN fibers or B_4C/BN/C fibers and monoliths, are outlined in a separate report.[12]

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Equation 1

$$B_{10}H_{14} + 2L: \longrightarrow L{\cdot}B_{10}H_{12}{\cdot}L + H_2$$

Equation 2

$$(Et_3N)_2B_{10}H_{12} \xrightarrow{110^oC} [Et_3NH]_2[B_{10}H_{10}]$$

$$[Et_3NH]_2[B_{10}H_{10}]\,(aq) \xrightarrow[-\ [Et_3NH][X]]{+\ \ [cat][X]} [cat]_2[B_{10}H_{10}]\ (\Downarrow)$$

Equation 3

$$x\ B_{10}H_{14} + x\ :L{\sim}{\sim}{\sim}L: \longrightarrow x\ H_2 + \{B_{10}H_{12}{\cdot}L{\sim}{\sim}{\sim}L\}_x$$

TABLE I. Pyrolysis of $B_{10}H_{12}$·2L Adducts and $[P^+]_2[B_{10}H_{10}]$ Salts.

Compound	Ceramic Yield, %[a]	Ceramic Composition, %[b]		
		B	C	P
$B_{10}H_{12}(Ph_2PH)_2$	83	23.17	60.75	13.71
$B_{10}H_{12}(Ph_3P)_2$	86	18.20	69.59	9.88
$B_{10}H_{12}(Ph_2PCl)_2$	73	20.62 Cl, 0.02	57.09	13.17
$B_{10}H_{12}(Ph_2POH)_2$	77	21.38 O, 10.57	55.65	11.93
$B_{10}H_{12}(Ph_2PN_3)_2$	72			
$B_{10}H_{12}(Ph_2PNHNH_2)_2$	71	27.69 N, 16.56	43.80	8.20
$B_{10}H_{12}(Bu_3P)_2$	58	35.94	46.34	35.94
$B_{10}H_{12}((Me_2N)_2PCl)_2$	55			
$[Ph_3PMe]_2[B_{10}H_{10}]$	83			
$[Ph_4P]_2[B_{10}H_{10}]$	93	6.87	73.06	13.01
$[Ph_3P(CH_2)_3PPh_3]$-$[B_{10}H_{10}]$	91	15.96	69.33	8.33
$[Bu_3PMe]_2[B_{10}H_{10}]$	68	30.10	49.03	11.96

[a] Pyrolysis to 1000°C under argon.

$$\text{Ceramic yield} = \frac{\text{wt. residue}}{\text{wt. sample pyrolyzed}} \times 100$$

[b] Compare with B_4C calcd: 21.74%C, 78.26%B.

Table II. $B_{10}H_{12}$·2L Binder Experiments 16.7% Binder (by weight)

$B_{10}H_{12}$·2L	Ceramic Powder	Mixture Method[a]	Color	Shape Retention
$B_{10}H_{12}[(C_6H_5)_2PH]_2$	B_4C	A	Black	Excellent
$B_{10}H_{12}[(C_6H_5)_2PCl]_2$	B_4C	A	Black	Excellent
$B_{10}H_{12}[(C_6H_5)_2PNHNH_2]_2$	B_4C	A	Black	Satisfactory
$B_{10}H_{12}[(C_6H_5)_2POH]_2$	B_4C	A	Black	Good
$B_{10}H_{12}[(C_6H_5)_2PN_3]_2$	B_4C	A	Black	Satisfactory
$B_{10}H_{12}\{[(CH_3)_2N]_2PCl\}_2$	B_4C	A	Black	Fair
$B_{10}H_{12}[(C_4H_9)_3P]_2$	B_4C	B(pentane)	Black	Good
$B_{10}H_{12}[(C_6H_5)_3P]_2$	B_4C	B(acetone)	Black	Excellent
$B_{10}H_{12}[(C_6H_5)_3P]_2$	B_4C	C(pentane)	Black	Excellent
$B_{10}H_{12}[(C_6H_5)_2PH]_2$	B_4C	B(acetone)	Black	Excellent
$B_{10}H_{12}[(C_6H_5)_2PH]_2$	B_4C	C(pentane)	Black	Excellent
$B_{10}H_{12}[(C_6H_5)_3P]_2$	B	A	Dk.Red	Excellent
$B_{10}H_{12}[(C_6H_5)_3P]_2$	Si_3N_4	A	Gray	Excellent
$B_{10}H_{12}[(C_6H_5)_3P]_2$	α-SiC	A	Dk.Gray	Good
$B_{10}H_{12}[(C_6H_5)_3P]_2$	β-SiC	A	Dk.Gray	Good
$B_{10}H_{12}[(C_6H_5)_3P]_2$	BN	A	Gray	Satisfactory
$B_{10}H_{12}[(C_6H_5)_3P]_2$	AlN	A	Silver/ Gray	Good
$B_{10}H_{12}[(C_6H_5)_3P]_2$	BP	A	Gray	Fair
$B_{10}H_{12}[(C_6H_5)_3P]_2$	$B_{13}P_2$	A	Dk.Gray	Excellent
$B_{10}H_{12}[(C_6H_5)_3P]_2$	Rayon	B(acetone)	Black	Good

[a]Solvent or diluent used in sample preparation.

TABLE III. $B_{10}H_{12}$·2L Binder Experiments (other weight fractions of binder)

$B_{10}H_{12}$·2L,#g	Ceramic Powder,#g	Mixture Method	Color	Shape Retention
$B_{10}H_{12}[(C_6H_5)_3P]_2$,3.0	none	A	Black	Good
$B_{10}H_{12}[(C_6H_5)_3P]_2$,0.1	B_4C,2.9	A	Black	Fair
$B_{10}H_{12}[(C_6H_5)_3P]_2$,0.1	B_4C,2.9	B(acetone)	Black	Fair
$B_{10}H_{12}[(C_6H_5)_3P]_2$,0.1	B_4C,2.9	C(pentane)	Black	Fair
$B_{10}H_{12}[(C_6H_5)_3P]_2$,0.25	B_4C,2.75	A	Black	Satisfactory
$B_{10}H_{12}[(C_6H_5)_3P]_2$,0.25	B_4C,2.75	B(acetone)	Black	Satisfactory
$B_{10}H_{12}[(C_6H_5)_3P]_2$,0.25	B_4C,2.75	C(pentane)	Black	Satisfactory
$B_{10}H_{12}[(C_6H_5)_2PH]_2$,0.1	B_4C,2.9	A	Black	Fair
$B_{10}H_{12}[(C_6H_5)_2PH]_2$,0.1	B_4C,2.9	B(acetone)	Black	Fair
$B_{10}H_{12}[(C_6H_5)_2PH]_2$,0.1	B_4C,2.9	C(pentane)	Black	Fair
$B_{10}H_{12}[(C_6H_5)_2PH]_2$,0.25	B_4C,2.75	A	Black	Fair
$B_{10}H_{12}[(C_6H_5)_2PH]_2$,0.25	B_4C,2.75	B(acetone)	Black	Fair
$B_{10}H_{12}[(C_6H_5)_2PH]_2$,0.25	B_4C,2.75	C(pentane)	Black	Fair

TABLE IV

PHOSPHORUS-CONTAINING POLYMERS INVESTIGATED AS CERAMIC PRECURSORS

POLYMER LINKER*	CERAMIC YIELD TO 1000°C	ELEMENTAL ANALYSIS OF CERAMIC		
		B	C	P
O	93	25.30 O, 12.05	52.01	8.69
O†	NA	28.90 O, 2.88	60.21	0.39
$N{=}PPh_2CH_2CH_2PPh_2{=}N$	52	22.75 N, 0.14	56.31	12.46
CH_2CH_2	92	22.52	45.78	11.25
C≡C	69	20.05	59.15	14.59
NHNH	57	not determined		

*All polymers have the following structural formula:

$$-\{B_{10}H_{12}\cdot Ph_2P-\text{linker}-PPh_2\}_x-$$

†Sample pyrolyzed to 1500°C

TABLE S1. EXPERIMENTAL

General Comments

All manipulations were done in an inert atmosphere (argon or nitrogen) following standard techniques. All solvents were distilled from appropriate drying agents under a nitrogen atmosphere prior to use. All reagents used were available from common suppliers and were used as received. All new compounds were fully characterized by spectroscopic (multinuclear NMR and IR) and analytical data. All compounds had NMR resonances (^{11}B, ^{13}C, ^{1}H, ^{31}P) and IR absorptions that were consistent with their formulated structures. Ceramic analyses were obtained from Galbraith Laboratories, Knoxville, Tenn., and C, H, N analyses on non-ceramic materials were obtained from Scandinavian Microanalytical Laboratory, Herlev, Denmark.

NMR measurements were obtained using a Varian XL300 NMR spectrometer. IR measurements were obtained on a Perkin-Elmer Model 1430 spectrometer. DRIFT spectra were recorded on an IBM Model IR/85 spectrometer. TMA and TGA measurements were obtained on a Perkin-Elmer TGS2 equipped with a Thermal Analysis System 4 controller. Lindberg tube furnaces with Eurotherm controllers were used for all bulk pyrolyses. For pyrolyses to 1000°C, 1 1/2" quartz tubes and fused silica boats were used for all samples (bars and bulk); for ones to 1500°C, 2 1/2" mullite tubes and boron nitride boats supported on alumina "dee" tubes were used. All pyrolyses were done under a flowing argon atmosphere, for runs to 1000°C the flow rate was ca. 6-8 l/hr, for runs to 1500°C it was ca. 16-20 l/hr.

A stainless steel die was used for forming 1 1/2" x 1/2" bars. A Carver laboratory press was used for uniaxial bar pressing. Isostatic bar pressing was done in a pneumatically-driven oil press with the bars contained in evacuated, sealed rubber bags. X-ray powder diffraction spectroscopy was obtained on a Charles Supper detector and Diano generator instrument.

Preparation of $[B_{10}H_{12}(Ph_3P)_2]$

A 250 ml Schlenk flask equipped with a stir-bar, gas inlet tube and a septum was charged (under argon) with 5.0 g (41 mmol) of $B_{10}H_{14}$, 35 ml of diethyl ether and a solution of 25.0 g (95 mmol) of Ph_3P in 150 ml of Et_2O (with vigorous stirring during and for 5 min after the addition). The precipitate which had formed was filtered, washed with Et_2O and dried at 100°C/0.1 mm Hg. The complexes where L = Ph_2PH, Ph_2PCl, Bu_3P, and $(Me_2N)_2PCl$, were prepared by this general procedure. Those where L = Ph_2POH, Ph_2PN_3, Ph_2PNHNH_2 and Ph_2PNH_2 were prepared as described in ref. 13. The results of their pyrolysis (i.e., their ceramic yield and composition) are given in Table I.

Preparation of $[Ph_4P]_2[B_{10}H_{10}]$

A solution of 2.00 g $[Et_3NH]_2[B_{10}H_{10}]$ (6.2 mmol) in 30 ml 9/1 water/ethanol was added to a solution of $[Ph_4P][Br]$ (6.00 g, 14.3 mmol) in 50 ml of the same solvent mixture, in a 125 ml Erlenmeyer flask. After the mixture had been stirred for 5 minutes, the precipitate was filtered, washed with water, 5 ml of cold (ca. -10°C) acetone and, finally, with ether. Drying at 60°C/0.1 mm Hg for 5 h gave a white solid. The following salts were all prepared by the above general metathesis route: $[Ph_3PMe]_2[B_{10}H_{10}]$, $[Bu_3PMe]_2[B_{10}H_{10}]$ and $[Ph_3PCH_2CH_2CH_2PPh_3][B_{10}H_{10}]$. The results of their pyrolysis are given in Table I.

Preparation of $+B_{10}H_{12}\cdot Ph_2PCH_2CH_2PPh_2+_x$

To a solution of 300 mg (2.45 mmol) of $B_{10}H_{14}$ in 50 ml of Et_2O (at 0°C under nitrogen) was added with stirring a solution of 1.0 g (2.5 mmol) of $Ph_2PCH_2CH_2PPh_2$ in 50 ml of toluene. The reaction mixture was allowed to warm to room temperature and stirred for 20 h. During this time a precipitate formed which was filtered. It was dissolved in acetone and reprecipitated by adding Et_2O. A similar procedure was used in the preparation of $+B_{10}H_{12}\cdot Ph_2PC{\equiv}CPPh_2+_x$, $+B_{10}H_{12}\cdot Ph_2PCH_2PPh_2+_x$ and $+B_{10}H_{12}\cdot Ph_2PCH_2CH_2CH_2PPh_2+_x$.

Preparation of $+B_{10}H_{12}\cdot Ph_2PNHNHPPh_2+_x$

To a suspension of 2.03 g (3.6 mmol) of $B_{10}H_{12}(Ph_2PCl)_2$ and 2.00 g (3.6 mmol) of $B_{10}H_{12}(Ph_2PNHNH_2)_2$ in 200 ml of acetone was added with stirring, under nitrogen, 10 ml of Et_3N over a period of 2-3 min at room temperature. The solution became clear and within about 5 min a fine white precipitate appeared. After 2 h the mixture was filtered. The acetone filtrate was evaporated to dryness to leave 4.55 g of light yellow powder. Recrystallization from acetone/diethyl ether gave 3.25 g of white crystals, mp 176-178°C (dec. with gas evolution).

Preparation of Ceramic Bars from Pure $+B_{10}H_{12}\cdot L\text{-}L+_x$ Polymers

The procedure used with $+B_{10}H_{12}\cdot Ph_2POPPh_2+_x$ is described as an example.

A 3.0 g sample of the polymer was finely powdered in a mortar and pestle (inert atmosphere box) and then placed in a 1/2" x 1 1/2" rectangular die. Uniaxial pressing in a Carver press to 5,000 pounds (5 min) was followed by ambient temperature isostatic pressing to 50,000 psi (15 min). The polymer bar thus obtained had the approximate dimensions 1/2" x 1 1/2" x 1/4".

The bar was introduced into a fused silica pyrolysis boat which then was inserted into a quartz tube that had been flushed with argon for 15 min. (The end of the quartz tube was connected to an oil bubbler). After ca. 5 min, the argon flow was reduced from ca. 100 ml/min to about 20-30 ml/min, and the quartz tube was placed in a Lindberg tube furnace and heated at a rate of 10°C/min to a temperature of 1000°C.

Preparation of Ceramic Composite Bars using $B_{10}H_{12}\cdot 2L$ Complexes as Binders.

Three procedures were used for sample preparation:

A. Weighed quantities (See Tables II and III) of $B_{10}H_{12}\cdot 2L$ and the ceramic powder were mixed and ground for 15 min in a mortar and pestle.

B. The $B_{10}H_{12}\cdot 2L$ (0.5 g) was dissolved in 50 ml of a solvent (usually acetone) and 2.5 g of ceramic powder added. The stoppered flask was ultrasonicated for 15 min.

Afterwards, the solvent was removed at 100°C and 0.1 mm Hg.

C. The $B_{10}H_{12}\cdot 2L$ (0.5 g) and the ceramic powder (2.5 g) were suspended in a non-solvent, usually pentane. Further processing was as in B above.

The samples thus prepared were placed in a 1/2" x 1 1/2" rectangular die and pressed in a Carver press to 5,000 pounds uniaxially (6,667 psi), removed to an ambient temperature isostatic press and further pressed to 50 K psi. The uniaxial pressing time duration was about 5 min and the isostatic pressing time duration was about 15 min. The resulting bar was pyrolyzed in a stream of argon to 1000°C (10°C per min heating rate, hold at 1000°C for 30 min). The pyrolyzed sample was handled in an inert atmosphere box. The results of the individual experiments are given in Tables II and III.

A ceramic bar is considered to be "excellent" if it is a uniform, black rectangular bond that has retained its shape (vs the bar before pyrolysis) in all three dimensions without undergoing any discernable shrinkage or bloating above the detectable level of 3-5% and if its strength is such that it cannot be broken manually without the aid of mechanical means (e.g., vise and pliers).

The data in Table III were obtained similarly, but different weight ratios of binder to ceramic powder were used. It would seem that the 0.167 weight fraction of binder used (0.5/0.5 + 2.5) in the Table II experiments gives better results.

Such bars also were prepared using B_4C powder and $\{B_{10}H_{12}\cdot L\text{-}L\}_x$ polymers as binders, specifically with those in which L-L= POP, PMP, PEP, PPP, and PCCP. All are classified as excellent.

LIST OF FIGURE CAPTIONS

FIGURE 1. Structure of Decaborane(14), $B_{10}H_{14}$.

FIGURE 2. Structure of the $B_{10}H_{12}{\cdot}2L$ Complexes.

FIGURE 3. Structure of $B_{10}H_{10}^{2-}$.

FIGURE 4. Mass and Volume Change *vs* Temperature Plot for POP Polymer.

FIGURE 5. Density *vs* Temperature Plot for POP Polymer.

Figure 1. Structure of Decaborane (14), $B_{10}H_{14}$

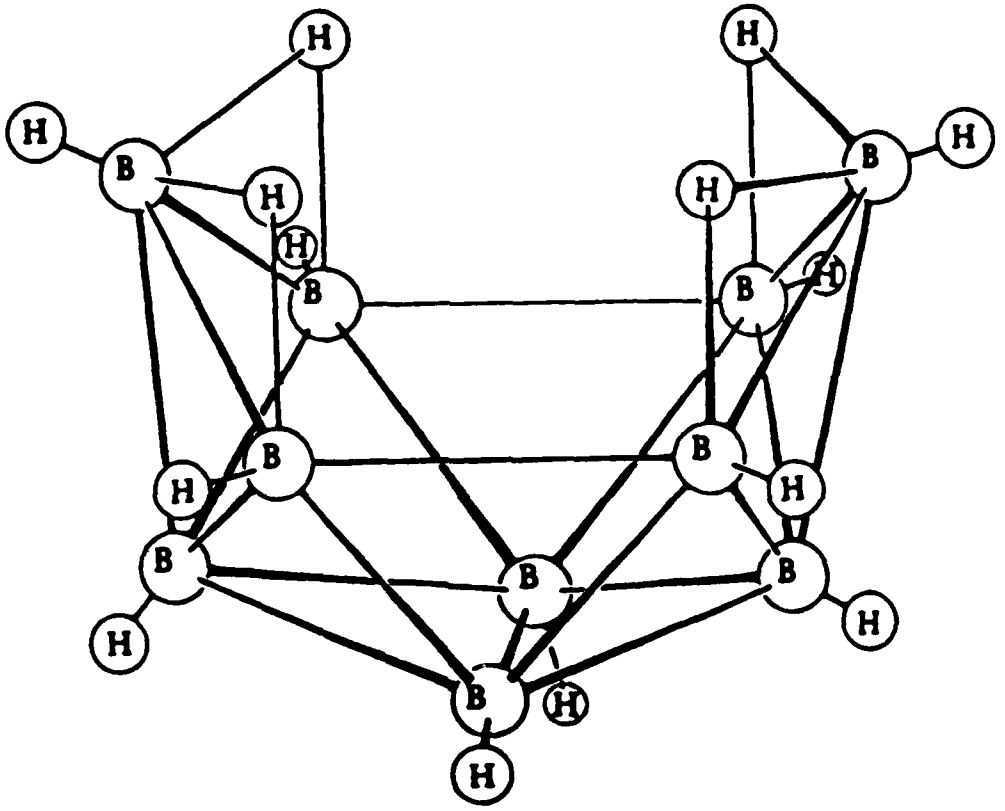


FIGURE 2.

Structure of the $B_{10}H_{12}\cdot 2L$ Complexes.

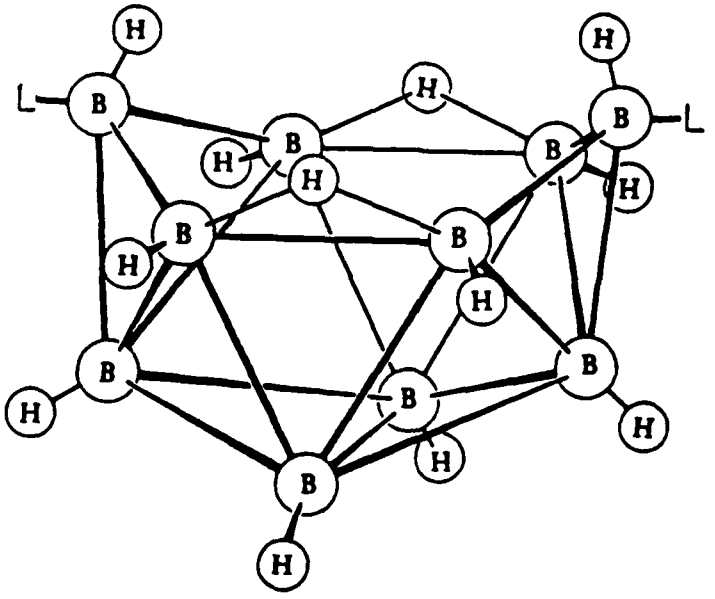


FIGURE 3

STRUCTURE OF $B_{10}H_{10}^{2-}$

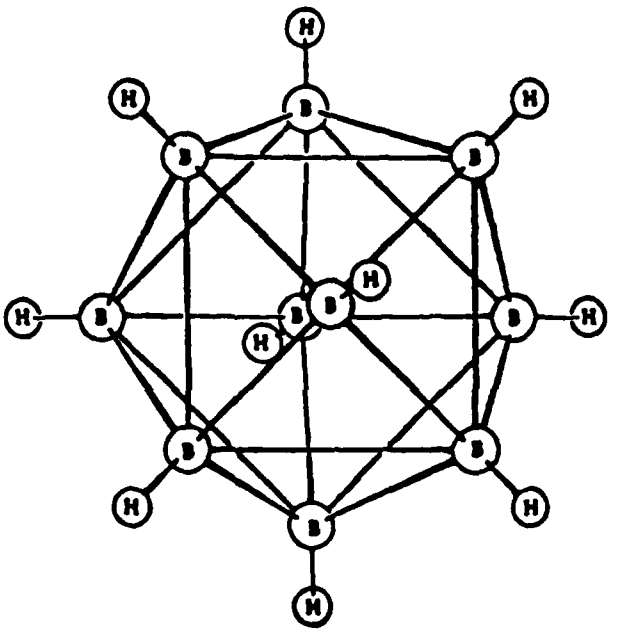


FIGURE 4

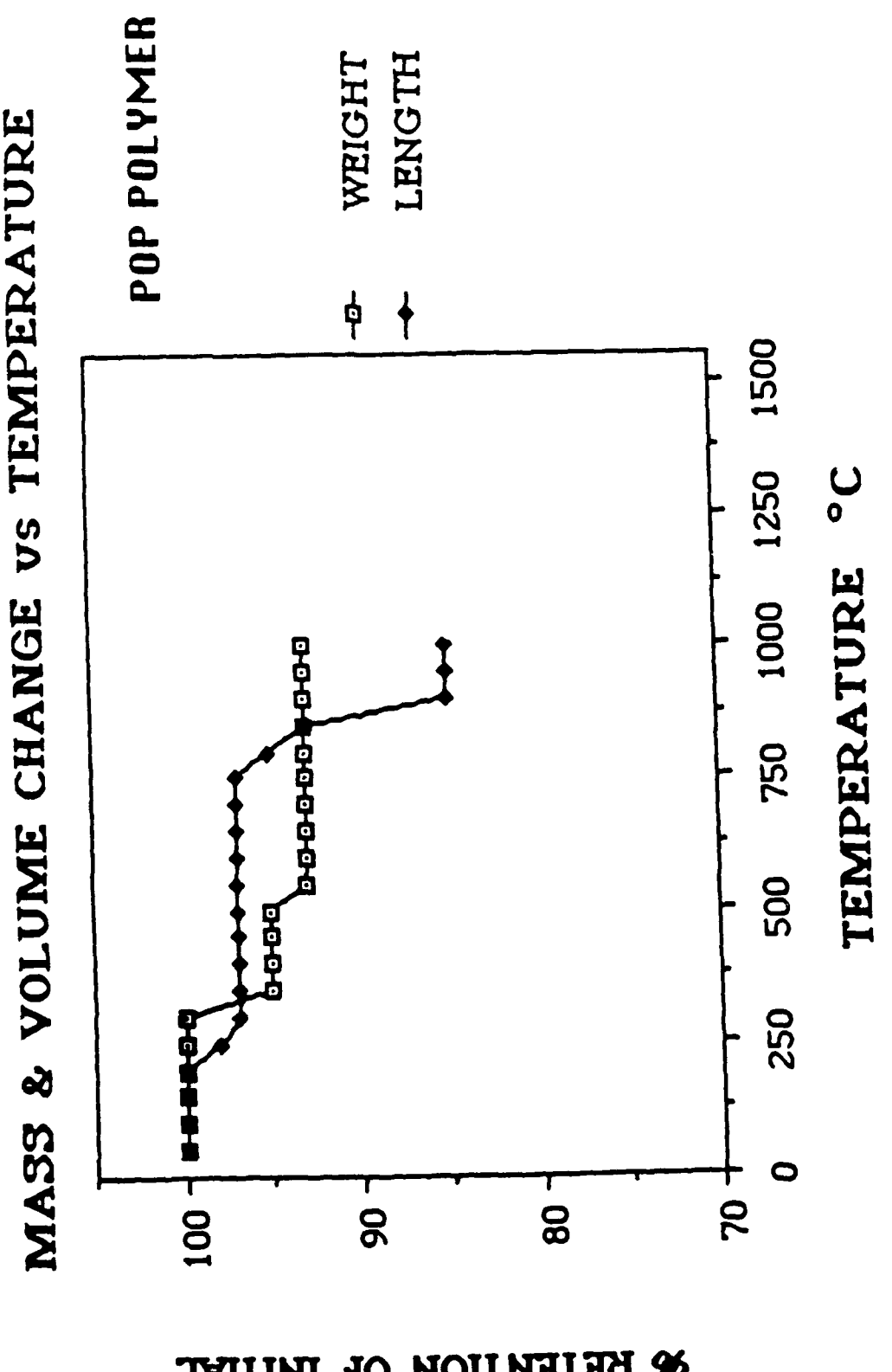
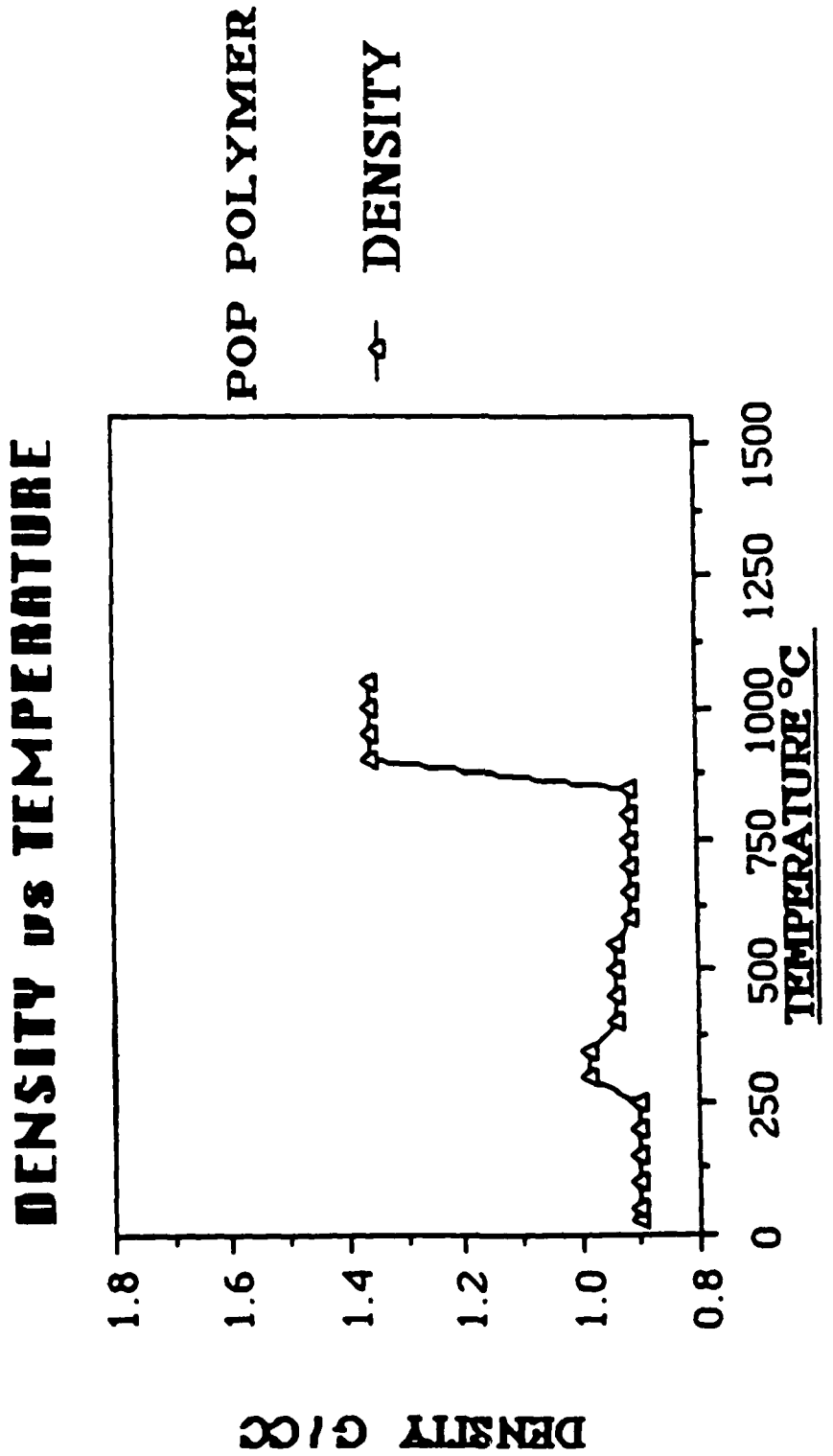

MASS & VOLUME CHANGE vs TEMPERATURE
POP POLYMER
WEIGHT
LENGTH
% RETENTION OF INITIAL
100
90
80
70
0
250
500
750
1000
1250
1500
TEMPERATURE °C

FIGURE 5


DENSITY vs TEMPERATURE
POP POLYMER
DENSITY
DENSITY G/CC
1.8
1.6
1.4
1.2
1.0
0.8
0
250
500
750
1000
1250
1500
TEMPERATURE °C

Phosphorus-Containing Derivatives of Decaborane(14) As Precursors to Boron-Containing Materials

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ABSTRACT

A route to soluble boron-containing polymers has been developed. The synthesis and characterization of phosphorus-containing monomeric and polymeric derivatives of $B_{10}H_{14}$ are given. Preparation and characterization of boron-containing ceramic materials from these molecular and macromolecular species are discussed. Success has been achieved in the areas of ceramic fiber and monolith production and in the area of binder applications for composites of advanced ceramic materials.

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